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PRODUCTION OF ALUMINUM MITRIDE SINTERED COMPACT

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Equivalents:

Abstract

PURPOSE:To obtain an AIN sintered compact excellent in thermal conductivity and mechanical strength at low cost in a practical way.

CONSTITUTION:AIN powder >=12.0m<2>/g in specific surface area is added with an oxygen-contg. and nonfluorine base rare earth metal compound as sintering auxiliary followed by molding, and the resultant form is then sintered in a nonoxidative atmosphere at <=1650 deg.C, thus obtaining the objective AIN sintered compact.

Cited Reference 2

6-191955

[Title of the Invention]

ALUMINUM NITRIDE SINTERED BODY PRODUCTION METHOD

[Abstract]

Object: To provide a practical method for economically producing an aluminum nitride sintered body excellent in thermal conductivity and mechanical strength.

Constitution: The present invention comprises firing a formed body obtained by adding a rare earth compound containing a non-fluoride type oxygen as a sintering aid to an aluminum nitride powder with a specific surface area of 12.0 m^2/g or more at a temperature of 1650°C or less in a non-oxidizing atmosphere.

[Claims]

1. An aluminum nitride sintered body production method which comprises firing a formed body obtained by adding a sintering aid to an aluminum nitride powder then forming, in a non-oxidizing atmosphere, thereby sintering the formed body, wherein

a specific surface area of the aluminum nitride powder is 12.0 m^2/g or more,

the sintering aid is a rare earth compound containing non-fluoride type oxygen, and

the firing in a non-oxidizing atmosphere is carried out at a temperature of 1650°C or less.

2. The aluminum nitride sintered body production method according to claim 1, wherein

reduction treatment is also carried out before or after or during the firing.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an aluminum nitride sintered body production method.

[0002]

[Prior Art]

Along with progress in highly advanced integration and high power of semiconductor devices such as IC, an electric insulating material with high heat releasing property has been desired. Under such circumstances, especially, an insulative substrate made of an aluminum nitride sintered body has been attracting attention and developed for practical use because of its excellent thermal conductivity, thermal expansion property, electric insulating property and the like.

[0003]

However, since an aluminum nitride powder, which is a raw material of the aluminum nitride sintered body, is costly, hard to be sintered and therefore necessitates firing at a high temperature of 1750°C or more, an aluminum nitride sintered body becomes extremely expensive. For that, aluminum nitride sintered body production methods to be carried out at a low cost by lowering the sintering temperature have been proposed. That

is, use of fluorides or oxides of rare earth elements in combination with fluorides or oxides of alkaline earth elements as sintering aids for aluminum nitride powders has been proposed (JP Kokai Sho 61-209959, USP 4,746,637). In these cases, aluminum nitride sintered bodies with high densities and high thermal conductivities are obtained by low temperature firing at 1550 to 1700°C. However, above-mentioned methods have the following problems.

[0004]

If a fluoride is used as a sintering aid, fluorine element generated by decomposition of such a sintering aid at the time of firing easily becomes a corrosive and toxic gas like HF and causes problem such as undesirable effects on health of workers and damages of a firing furnace and the like; therefore, such a fluoride is not practical to be used. As compared with a case of using a rare earth compound solely, combination use of a rare earth compound and an alkaline earth compound as a sintering aid is found effective to lower the liquid-phase formation temperature and, accordingly, makes low temperature firing possible. However, at the same time, grains significantly grow owing to liquid-phase formation and that results in degradation of the mechanical strength in spite of increase of heat conductivity. Further, in the case of an alkaline earth element, there are problems such as an easy occurrence of diffusion during firing to cause uneven distribution in a sintered body, uneven firing of an aluminum nitride sintered body, and deposition reaction on a firing furnace and a setter, which is of a jig and the like, is caused to result in their deterioration. Additionally, since the above-mentioned liquid phase forms thick grain

boundary layers and surrounds grains, the fracture mode becomes intergranular fracture. Generally, the mechanical strength is decreased as compared with the case of using solely a rare earth compound. For example, in the case of using Y_2O_3 alone, a liquid phase is formed between Al_2O_3 and Y_2O_3 at 1760°C and the liquid phase wets aluminum nitride grains but does not form grain boundary layers and the liquid phase is easily concentrated on triple points of grain boundaries to make grain boundary layers extremely thin and accordingly, the fracture mode is not attributed to intergranular fracture but more easily attributed to intragranular fracture. As compared with the intergranular fracture, the intragranular fracture results generally in higher mechanical strength.

[0005]

[Problems to be Solved by the Invention]

In consideration of the above-mentioned circumstances, an object of the present invention is to provide a practical method capable of economically producing an economical aluminum nitride sintered body excellent in thermal conductivity and mechanical strength.

[0006]

[Means for Solving the Problems]

In order to solve the above-mentioned problems, in an aluminum nitride sintered body production method according to the present invention, when firing a formed body obtained by adding a sintering aid to an aluminum nitride powder then forming, in a non-oxidizing atmosphere, thereby sintering the formed body, a specific surface area of the aluminum nitride powder is 12.0 m^2/g or more, the sintering aid is a non-fluoride type

oxygen containing rare earth compound, and the firing in a non-oxidizing atmosphere is carried out at a temperature of 1650°C or less.

[0007]

With respect to this invention, as it will be described later in detail, an embodiment in which reduction treatment is carried out before or after or during the firing is effective to increase the thermal conductivity of an obtained aluminum nitride sintered body (hereinafter, referred to as "AlN sintered body") and can be said to be an effective embodiment. In the present invention, the reason for using an aluminum nitride powder (hereinafter, referred to as "AlN powder") having a small particle diameter with a specific surface area of 12.0 m^2/g or more is because it is made possible to carry out sintering by low temperature firing at 1650°C or less in the condition of using solely a rare earth compound containing non-fluoride type oxygen (an oxygen-containing compound of rare earth elements), that is, a rare earth compound belonging to a group of rare earth oxides and non-fluoride type rare earth compounds to be rare earth oxides by firing.

[0008]

As described above, use of fluorides or oxides of rare earth elements in combination with fluorides or oxides of alkaline earth elements makes sintering of even an AlN powder with a specific surface area of less than 12.0 m^2/g possible; however, problems such as decrease of mechanical strength owing to grain growth, uneven firing of a resulting AlN sintered body, deteriorations of a firing furnace and a setter are caused. The present invention solves such adverse effects of the above-mentioned combination use and makes sintering by low temperature firing possible

with no need of combination use of sintering aids.

[0009]

For example, in the case of Y_2O_3, which is a typical oxygen-containing compound of rare earth elements, an eutectoid melted liquid is formed from Y_2O_3 and Al_2O_3 on the surface of AlN powder at 1760°C or more and for carrying out liquid-phase sintering, it is required to carry out firing at a temperature equal to or more than that temperature. Based on the investigations by the inventors, if Y_2O_3 is used alone for carrying out sintering a coarse AlN powder with a specific surface area of about 3.0 m^2/g, the above-mentioned liquid-phase sintering is indispensable and high temperature firing at 1760°C or higher is essentially required. Therefore, the inventors have made further investigations and found that not the liquid-phase sintering but solid-phase sintering seems to be possible and the firing temperature can be decreased if an AlN powder is a fine powder with a specific surface area of 12.0 m^2/g or more. It is found that in the case of an AlN powder with a specific surface area less than 1.20 m^2/g, sintering temperature exceeding 1700°C is required, whereas in the case of an AlN powder with a specific surface area of 12.0 m^2/g or more, sintering is made possible by firing at a temperature of 1650°C or less by using only a sintering aid of a non-fluoride type rare earth compound.

[0010]

When sintering is possible by firing at a temperature of 1650°C or less, it results in advantages reflected in the firing cost down. Practically, the life of a costly BN container employed as a firing container can be remarkably prolonged and, further, it is made possible to utilize an

economical alumina-based container in place of the costly BN container. The economical alumina-based container has been conventionally impossible to use because deformation by high temperature creep has become significant by firing at a temperature exceeding 1650°C. Furthermore, power consumption can be saved to result in cost down in terms of running cost of a firing furnace.

[0011]

Next, thermal conductivity and mechanical strength of an AlN sintered body to be obtained by the present invention will be described. As seen above, in the case of the present invention, since sintering of a fine AlN powder with a specific surface area of 12.0 m^2/g or more is carried out by firing at a temperature of 1650°C or less using only a sintering aid of a non-fluoride type rare earth compound, the sintering mechanism is supposedly not based on the liquid-phase sintering but on the solid-phase sintering. Accordingly, the grain size of an obtained AlN sintered body becomes smaller than that of an AlN sintered body obtained by using an alkaline earth compound which forms the liquid-phase even at 1650°C or less as a sintering aid and, as a result, the mechanical strength is increased. Nevertheless, in general, the smaller the grain size of an AlN sintered body becomes, the lower the thermal conductivity tends to be. Because the thermal conduction mechanism of an AlN sintered body is phonon conduction and the phonon conduction easily causes scattering in the grain boundaries and there are many grain boundaries in the case of an AlN sintered body with a small grain size; therefore, the phonon scattering becomes significant and thermal conduction is interfered.

[0012]

Further, impurity oxygen in an AlN powder that is a cause of thermal conductivity decrease is generally increased more when the specific surface area of the AlN powder is increased more (the particle diameter becomes smaller). That is, impurity oxygen exists in the surface layer of the AlN powder. Accordingly, in the case of the present invention where a fine AlN powder with a specific surface area of 12.0 m^2/g or more, the impurity oxygen amount inevitably increases as compared with that of a case of using an AlN powder having a larger particle diameter.

[0013]

In such a manner, an AlN sintered body obtained by the present invention is disadvantageous in terms of thermal conductivity attributed to that the grain size is small and impurity oxygen amount in an AlN powder as a raw material is high. However, when reduction treatment is carried out before or after or during firing in the present invention, the thermal conductivity can be improved. The reduction treatment decreases the amount of the impurity oxygen in the AlN powder and increases the thermal conductivity to the corresponding extent. Incidentally, since the grain size of the sintered body is scarcely changed by the reduction treatment, it is supposed that the decrease of the thermal conductivity relevant to the grain size is not at all solved, but some of oxygen in the surface layer of the AlN powder is taken in the gains of aluminum nitride at the time of sintering because of decrease of the oxygen amount and, accordingly, the thermal conductivity of the grains themselves is improved. As a result, it can be expected that the decrease of the thermal conductivity relevant to the grain

size is solved to some extent. As described above, in the case of performing also the reduction treatment, although the grain size is small, a high thermal conductivity can be achieved by improvement of the purity.

[0014]

The above descriptions can be summarized as follows. In the present invention, in order to carry out sintering by a low temperature firing at 1650°C or less, which makes economical firing possible, without using an alkaline earth compound or a fluoride type sintering aid that cause various problems, a finely granular AlN powder with a specific surface area of 12 m^2/g or more and an oxygen-containing compound of rare earth elements as raw materials. As a result, since the gain size in a sintered body becomes smaller than the case of using an alkaline earth compound, the mechanical strength can be improved. Further, with respect to the thermal conductivity, it is made possible to improve the thermal conductivity by reduction of impurity oxygen in an AlN powder by employing the reduction treatment.

[0015]

Examples of a non-fluoride type rare earth compound (oxygen-containing compound of rare earth elements) to be used as a sintering aid include oxides of rare earth elements such as Y, La, Dy, Er, Ce, Sm, Pm, Nd, Eu, Gd, Tb, Pr, Tm, Lu, Ho and Yb, and as compounds to be rare earth oxides by firing, carbonates, nitrates, hydroxides, and oxalates of these elements. In the case of using the sintering aid, a plurality of types of the rare earth oxides may be used in combination or a plurality of type of compounds to be the rare earth oxides by firing may be used in combination

or the rare earth oxides and compounds to be the rare earth oxides by firing may be used in combination. With respect to the addition amount of the sintering aid, it is preferable to adjust the amount of the sintering aid to be 0.1 to 10% by weight in 100% by weight of the entire body of the obtained AlN sintered body.

[0016]

Firing is carried out at a temperature in a range of 1400 to 1650°C for about 1 to 6 hours; however, the conditions are not limited to these ranges. The reduction treatment may be carried out either before or after or during firing for sintering; however, oxygen is easier to be removed before sintering is promoted far extent. For example, in the case of sintering at 1650°C, firing at a temperature up to 1200°C may be carried out in reducing atmosphere and, after that, in neutral atmosphere. Alternatively, firing may be carried out entirely in reducing atmosphere to simultaneously carry out sintering and reduction treatment in parallel for almost same period. Examples of the reducing atmosphere to be employed for the reduction treatment include reducing atmosphere of H_3, CO, NH_3, CH_4, C_2H_4, C_2H_6, C_3H_8 and the like, and combination of these reducing gases with neutral gas atmosphere of N_2, Ar or the like provides effective treatment atmosphere. Further, in the case a firing furnace is a carbon furnace employing a carbon heater or a carbon furnace material, reducing atmosphere of vapor phase carbon can be easily generated.

[0017]

[Operations]

In the case of the present invention, an AlN powder with a specific

surface area of less than 12.0 m^2/g can be sintered by firing at a temperature as low as 1,650°C or lower using only a sintering aid of a non-fluoride type rare earth compound without using an alkaline earth compound and a fluoride type sintering aid that cause various problems.

[0018]

Since neither alkaline earth compound nor fluoride type sintering aid is used, uneven firing and warping of an AlN sintered body, and deterioration of a furnace and a setter due to diffusion can be inhibited. Moreover, since firing is carried out at a low temperature of 1650°C or less, the life of a firing container can be prolonged and an economical material is made applicable and also, the power consumption can be saved to result in running cost down.

[0019]

Further, since the grain size in an obtained AlN sintered body becomes small, the mechanical strength can be improved: inhibited and since firing is carried out at a low temperature of 1650°C or less, the life of a firing container can be prolonged and an economical material is made applicable and also, the power consumption can be saved to result in running cost down.

[0020]

In the case reduction treatment is carried out before or after or during the firing, owing to removal of impurity oxygen and the like, a highly thermally conductive AlN sintered body can be obtained.

[0021]

[Examples]

Hereinafter, examples of the present invention will be described. The present invention is not limited to the following examples.

Example 1

As a sintering aid, 3.0% by weight of Y_2O_3 was added to an AlN powder with a specific surface area of 12.0 m^2/g, and mixed by a wet type ball mill. The obtained mixture was dried and granulated, then formed into a disk shape with a diameter of 20 mm and a height of 10 mm by a uniaxial press, and further subjected to CIP with a pressure of 1.5 ton/cm^2 to obtain a disk-shaped formed body.

[0022]

Successively, the obtained formed body was set in a crucible made of BN, covered with a loose cover made of BN, and the crucible was housed in a carbon furnace. While N_2 gas containing 4% of H_2 being circulated, the temperature was raised to 120°C and the gas was changed to 100% N_2. The temperature was further raised to 1650°C and kept for 3 hours to obtain an AlN sintered body.

Example 2

An AlN sintered body was obtained in the same manner as Example 1, except that Y_2O_3 as a sintering aid was replaced by $Y(NO_3)_3$ and the sintering temperature was changed to be 1600°C.

[0023]

Example 3

As a sintering aid, 3.0% by weight of Y_2O_3 was added to an AlN powder with a specific surface area of 15.0 m^2/g and a disk-shaped formed body was obtained in the same manner as Example 1. After that, the

formed body was put in an alumina setter, covered with an aluminum plate and housed in a carbon furnace. While N_2 gas containing 4% of H_2 being circulated, the temperature was raised to 1600°C and kept for 3 hours to obtain an AlN sintered body. N_2 gas containing 4% of H_2 was used for the entire process.

[0024]

Example 4

An AlN sintered body was obtained in the same manner as Example 3, except that Y_2O_3 as a sintering aid was replaced by La_2O_3.

Example 5

An AlN sintered body was obtained in the same manner as Example 3, except that the crucible made of BN and a cover made of BN used in Example 1 were used in place of the alumina setter and the alumina plate, and 100% N_2 was used for the entire process.

[0025]

Comparative Example 1

As a sintering aid, 3.0% by weight of Y_2O_3 was added to an AlN powder with a specific surface area of 10.0 m^2/g and a disk-shaped formed body was obtained in the same manner as Example 1. After that, the formed body was put in a crucible made of BN, covered with a loose cover made of BN, and housed in a carbon furnace. While 100 % N_2 gas being circulated, the temperature was raised to 1650°C and kept for 3 hours to obtain an AlN sintered body.

[0026]

Comparative Example 2

An AlN sintered body was obtained in the same manner as Comparative Example 1, except that 3.0% by weight of Y_2O_3 and 0.5% by weight of CaO were added as the sintering aid.

Comparative Example 3

An AlN sintered body was obtained in the same manner as Comparative Example 2, except that an AlN powder with a specific surface area of 3.0 m^2/g was used as the AlN powder.

[0027]

Tables 1 and 2 show the main firing conditions of the respective Examples and Comparative Examples, and the densities, the grain sizes, the thermal conductivities and the bending strength of the respective AlN sintered bodies obtained in Examples and Comparative Examples.

[0028]

[Table 1]

	Type and amount of sintering aid (% by weight)	Firing temperature and duration °C, Hr	Atmosphere at firing	Material of container for firing
Example 1	Y_2O_3 3% by weight	1650 3	1200°C or less: $H_2 + N_2$ * 1200°C or more: N_2	BN
Example 2	$Y(NO_3)_3$ 3% by weight	1600 3	1200°C or less: $H_2 + N_2$ * 1200°C or more: N_2	BN
Example 3	Y_2O_3 3% by weight	1600 3	$H_2 + N_2$ *	Al_2O_3
Example 4	La_2O_3 3% by weight	1600 3	$H_2 + N_2$ *	Al_2O_3
Example 5	Y_2O_3 3% by weight	1600 3	N_2	BN
Comparative Example 1	Y_2O_3 3% by weight	1650 3	N_2	BN
Comparative Example 2	Y_2O_3 3% by weight CaO 0.5% by weight	1650 3	N_2	BN
Comparative Example 3	Y_2O_3 3% by weight CaO 0.5% by weight	1650 3	N_2	BN

*: N_2 gas containing 4% of H_2

[0029]

[Table 2]

	Density (g/cm^3)	Thermal conductivity (W/mK)	Bending strength (kgf/mm^2)	Average grain size	Specific surface area of AlN powder
Example 1	3.30	150	44	0.9 μm	12 m^2/g
Example 2	3.29	143	46	0.8 μm	12 m^2/g
Example 3	3.30	135	48	0.7 μm	15 m^2/g
Example 4	3.33	130	47	0.7 μm	15 m^2/g
Example 5	3.30	120	50	0.7 μm	15 m^2/g
Comparative Example 1	2.87	100	25	1.0 μm	10 m^2/g
Comparative Example 2	3.23	115	28	1.4 μm	10 m^2/g
Comparative Example 3	3.10	108	23	1.5 μm	3 m^2/g

[0030]

As shown in Table 2, the AlN sintered bodies of Examples were sufficiently densified without using an alkaline earth type or fluoride type sintering aid and provided with both high thermal conductivities and bending strength. On the contrary, AlN sintered bodies of Comparative Examples were not provided with those properties.

[0031]

[Effects of the Invention]

In an AlN sintered body production method according to the present invention, firing is carried out at a low temperature of not more than 1650°C, therefore the life of a container for a firing jig can be prolonged and it is made possible to utilize a container made of an economical material and further power consumption can be saved to result in cost down of running cost as well. Furthermore, since neither alkaline earth compound nor fluoride type sintering aid is required to be used, uneven firing, warping, and deterioration of a furnace and a setter owing to diffusion can be prevented and further the grain size becomes small to give AlN sintered bodies excellent in mechanical strength at a low cost. In addition, in the case reduction treatment is carried out, the thermal conductivities of AlN sintered bodies can be improved. Accordingly, the present invention is practical and remarkably advantageous for practical application.

[Written Amendment]

[Date of Submission] February 24, 1993

[Written Amendment 1]

[Title of Object Document of Amendment] Specification

[Title of Object Item of Amendment] The whole sentence

[Method for Amendment] Replacement

[Contents of Amendment]

[Title of Document] Specification

[Title of the Invention]

ALUMINUM NITRIDE SINTERED BODY PRODUCTION METHOD

[Claims]

1. An aluminum nitride sintered body production method which comprises firing a formed body obtained by adding a sintering aid to an aluminum nitride powder then forming, in a non-oxidizing atmosphere, thereby sintering the formed body, wherein

a specific surface area of the aluminum nitride powder is 12.0 m^2/g or more,

the sintering aid is a rare earth compound containing non-fluoride type oxygen, and

the firing in a non-oxidizing atmosphere is carried out at a temperature of 1650°C or less.

2. The aluminum nitride sintered body production method according to claim 1, wherein

reduction treatment is also carried out before or after or during the firing.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an aluminum nitride sintered body production method.

[0002]

[Prior Art]

Along with progress in highly advanced integration and high power of semiconductor devices such as IC, an electric insulating material with high heat releasing property has been desired. Under such circumstances, especially, an insulative substrate made of an aluminum nitride sintered body has been attracting attention and developed for practical use because of its excellent thermal conductivity, thermal expansion property, electric insulating property and the like.

[0003]

However, since an aluminum nitride powder, which is a raw material of the aluminum nitride sintered body, is costly, hard to be sintered and therefore necessitates firing at a high temperature of 1750°C or more, an aluminum nitride sintered body becomes extremely expensive. For that, aluminum nitride sintered body production methods to be carried out at a low cost by lowering the sintering temperature have been proposed. That is, use of fluorides or oxides of rare earth elements in combination with fluorides or oxides of alkaline earth elements as sintering aids for aluminum nitride powders has been proposed (JP Kokai Sho 61-209959, USP 4,746,637). In these cases, aluminum nitride sintered bodies with high

densities and high thermal conductivities are obtained by low temperature firing at 1550 to 1700°C. However, above-mentioned methods have the following problems.

[0004]

If a fluoride is used as a sintering aid, fluorine element generated by decomposition of such a sintering aid at the time of firing easily becomes a corrosive and toxic gas like HF and causes problem such as undesirable effects on health of workers and damages of a firing furnace and the like; therefore, such a fluoride is not practical to be used. As compared with a case of using a rare earth compound solely, combination use of a rare earth compound and an alkaline earth compound as a sintering aid is found effective to lower the liquid-phase formation temperature and, accordingly, makes low temperature firing possible. However, at the same time, grains significantly grow owing to liquid-phase formation and that results in degradation of the mechanical strength in spite of increase of heat conductivity. Further, in the case of an alkaline earth element, there are problems such as an easy occurrence of diffusion during firing to cause uneven distribution in a sintered body, uneven firing of an aluminum nitride sintered body, and deposition reaction on a firing furnace and a setter, which is of a jig and the like, is caused to result in their deterioration. Additionally, since the above-mentioned liquid phase forms thick grain boundary layers and surrounds grains, the fracture mode becomes intergranular fracture. Generally, the mechanical strength is decreased as compared with the case of using solely a rare earth compound. For example, in the case of using Y_2O_3 alone, a liquid phase is formed between

Al_2O_3 and Y_2O_3 at 1760°C and the liquid phase wets aluminum nitride grains but does not form grain boundary layers unlike the case of using an alkaline earth compound that forms thick grain boundary layers, and the liquid phase is easily concentrated on triple points of grain boundaries to make grain boundary layers extremely thin and accordingly, the fracture mode is not attributed to intergranular fracture but more easily attributed to intragranular fracture. As compared with the intergranular fracture, the intragranular fracture results generally in higher mechanical strength.

[0005]

[Problems to be Solved by the Invention]

In consideration of the above-mentioned circumstances, an object of the present invention is to provide a practical method capable of economically producing an economical aluminum nitride sintered body excellent in thermal conductivity and mechanical strength.

[0006]

[Means for Solving the Problems]

In order to solve the above-mentioned problems, in an aluminum nitride sintered body production method according to the present invention, when firing a formed body obtained by adding a sintering aid to an aluminum nitride powder then forming, in a non-oxidizing atmosphere, thereby sintering the formed body, a specific surface area of the aluminum nitride powder is 12.0 m^2/g or more, the sintering aid is a non-fluoride type oxygen containing rare earth compound, and the firing in a non-oxidizing atmosphere is carried out at a temperature of 1650°C or less.

[0007]

With respect to this invention, as it will be described later in detail, an embodiment in which reduction treatment is carried out before or after or during the firing is effective to increase the thermal conductivity of an obtained aluminum nitride sintered body (hereinafter, referred to as "AlN sintered body") and can be said to be an effective embodiment. In the present invention, the reason for using an aluminum nitride powder (hereinafter, referred to as "AlN powder") having a small particle diameter with a specific surface area of 12.0 m^2/g or more is because it is made possible to carry out sintering by low temperature firing at 1650°C or less in the condition of using solely a rare earth compound containing non-fluoride type oxygen (an oxygen-containing compound of rare earth elements), that is, a rare earth compound belonging to a group of rare earth oxides and non-fluoride type rare earth compounds to be rare earth oxides by firing.

[0008]

As described above, use of fluorides or oxides of rare earth elements in combination with fluorides or oxides of alkaline earth elements makes sintering of even an AlN powder with a specific surface area of less than 12.0 m^2/g possible; however, problems such as decrease of mechanical strength owing to grain growth, uneven firing of a resulting AlN sintered body, deteriorations of a firing furnace and a setter are caused. The present invention solves such adverse effects of the above-mentioned combination use and makes sintering by low temperature firing possible with no need of combination use of sintering aids.

[0009]

For example, in the case of Y_2O_3, which is a typical

oxygen-containing compound of rare earth elements, an eutectoid melted liquid is formed from Y_2O_3 and Al_2O_3 on the surface of AlN powder at 1760°C or more and for carrying out liquid-phase sintering, it is required to carry out firing at a temperature equal to or more than that temperature. Based on the investigations by the inventors, if Y_2O_3 is used alone for carrying out sintering a coarse AlN powder with a specific surface area of about 3.0 m^2/g, the above-mentioned liquid-phase sintering is indispensable and high temperature firing at 1760°C or higher is essentially required. Therefore, the inventors have made further investigations and found that not the liquid-phase sintering but solid-phase sintering seems to be possible and the firing temperature can be decreased <u>if the particle diameter of an AlN powder is made further finer</u>. It is found that in the case of an AlN powder with a specific surface area less than 1.20 m^2/g, sintering temperature exceeding 1700°C is required, whereas in the case of an AlN powder with a specific surface area of 12.0 m^2/g or more, sintering is made possible by firing at a temperature of 1650°C or less by using only a sintering aid of a non-fluoride type rare earth compound.

[0010]

When sintering is possible by firing at a temperature of 1650°C or less, it results in advantages reflected in the firing cost down. Practically, the life of a costly BN container employed as a firing container can be remarkably prolonged and, further, it is made possible to utilize an economical alumina-based container in place of the costly BN container. The economical alumina-based container has been conventionally impossible to use because deformation by high temperature creep has become

significant by firing at a temperature exceeding 1650°C. Furthermore, power consumption can be saved to result in cost down in terms of running cost of a firing furnace.

[0011]

Next, thermal conductivity and mechanical strength of an AlN sintered body to be obtained by the present invention will be described. As seen above, in the case of the present invention, since sintering of a fine AlN powder with a specific surface area of 12.0 m^2/g or more is carried out by firing at a temperature of 1650°C or less using only a sintering aid of a non-fluoride type rare earth compound, the sintering mechanism is supposedly not based on the liquid-phase sintering but on the solid-phase sintering. Accordingly, the grain size of an obtained AlN sintered body becomes smaller than that of an AlN sintered body obtained by using an alkaline earth compound which forms the liquid-phase even at 1650°C or less as a sintering aid and, as a result, the mechanical strength is increased. Nevertheless, in general, the smaller the grain size of an AlN sintered body becomes, the lower the thermal conductivity tends to be. Because the thermal conduction mechanism of an AlN sintered body is phonon conduction and the phonon conduction easily causes scattering in the grain boundaries and there are many grain boundaries in the case of an AlN sintered body with a small grain size; therefore, the phonon scattering becomes significant and thermal conduction is interfered.

[0012]

Further, impurity oxygen in an AlN powder that is a cause of thermal conductivity decrease is generally increased more when the specific

surface area of the AlN powder is increased more (the particle diameter becomes smaller). That is, impurity oxygen easily exists in the surface layer of the AlN powder. Accordingly, in the case of the present invention where a fine AlN powder with a specific surface area of 12.0 m^2/g or more, the impurity oxygen amount inevitably increases as compared with that of a case of using an AlN powder having a larger particle diameter.

[0013]

In such a manner, an AlN sintered body obtained by the present invention is disadvantageous in terms of thermal conductivity attributed to that the grain size is small and impurity oxygen amount in an AlN powder as a raw material is high. However, when reduction treatment is carried out before or after or during firing in the present invention, the thermal conductivity can be improved. The reduction treatment decreases the amount of the impurity oxygen in the AlN powder and increases the thermal conductivity to the corresponding extent. That is, even if impurity oxygen is decreased, basically, the grain size of the sintered body is scarcely changed; therefore, it is nevertheless disadvantageous for solution of thermal conductivity decrease attributed to the grain size, that is, for improvement of heat conduction. However, on the other hand, decrease of the thermal conductivities of AlN grains themselves attributed to that some of oxygen in the surface layer of the AlN grains is taken in the intra-AlN gains at the time of sintering can be moderated by decrease of the oxygen amount by the reduction treatment. As a result, although the grain size is small, high thermal conductivity can be achieved by improving the purity and, accordingly, it results in solution of the decrease of the thermal

conductivity attributed to the grain size.

[0014]

The above descriptions can be summarized as follows. In the present invention, in order to carry out sintering by a low temperature firing at 1650°C or less, which makes economical firing possible, without using an alkaline earth compound or a fluoride type sintering aid that cause various problems, a finely granular AlN powder with a specific surface area of 12 m^2/g or more and an oxygen-containing compound of rare earth elements as raw materials. As a result, since the gain size in a sintered body becomes smaller than the case of using an alkaline earth compound, the mechanical strength can be improved. Further, with respect to the thermal conductivity, it is made possible to improve the thermal conductivity by reduction of impurity oxygen in an AlN powder by employing the reduction treatment.

[0015]

Examples of a non-fluoride type rare earth compound (oxygen-containing compound of rare earth elements) to be used as a sintering aid include oxides of rare earth elements such as Y, La, Dy, Er, Ce, Sm, Pm, Nd, Eu, Gd, Tb, Pr, Tm, Lu, Ho and Yb, and as compounds to be rare earth oxides by firing, carbonates, nitrates, hydroxides, and oxalates of these elements. In the case of using the sintering aid, a plurality of types of the rare earth oxides may be used in combination or a plurality of type of compounds to be the rare earth oxides by firing may be used in combination or the rare earth oxides and compounds to be the rare earth oxides by firing may be used in combination. With respect to the addition amount of the

sintering aid, it is preferable to adjust the amount of the sintering aid to be 0.1 to 10% by weight in 100% by weight of the entire body of the obtained AlN sintered body.

[0016]

Firing is carried out at a temperature in a range of 1400 to 1650°C for about 1 to 6 hours; however, the conditions are not limited to these ranges. The reduction treatment may be carried out either before or after or during firing for sintering; however, oxygen is easier to be removed before sintering is promoted far extent. For example, in the case of sintering at 1650°C, firing at a temperature up to 1200°C may be carried out in reducing atmosphere and, after that, in neutral atmosphere. Alternatively, firing may be carried out entirely in reducing atmosphere to simultaneously carry out sintering and reduction treatment in parallel for almost same period. Examples of the reducing atmosphere to be employed for the reduction treatment include reducing atmosphere of H_3, CO, NH_3, CH_4, C_2H_4, C_2H_6, C_3H_8 and the like, and combination of these reducing gases with neutral gas atmosphere of N_2, Ar or the like provides effective treatment atmosphere. Further, in the case a firing furnace is a carbon furnace employing a carbon heater or a carbon furnace material, reducing atmosphere of vapor phase carbon can be easily generated.

[0017]

[Operations]

In the case of the present invention, an AlN powder with a specific surface area of less than 12.0 m^2/g <u>or more</u> can be sintered by firing at a temperature as low as 1,650°C or lower using only a sintering aid of a

non-fluoride type rare earth compound without using an alkaline earth compound and a fluoride type sintering aid that cause various problems.

[0018]

Since neither alkaline earth compound nor fluoride type sintering aid is used, uneven firing and warping of an AlN sintered body, and deterioration of a furnace and a setter due to diffusion can be inhibited. Moreover, since firing is carried out at a low temperature of 1650°C or less, the life of a firing container can be prolonged and an economical material is made applicable and also, the power consumption can be saved to result in running cost down.

[0019]

Further, since the grain size in an obtained AlN sintered body becomes small, the mechanical strength can be improved.

[0020]

In the case reduction treatment is carried out before or after or during the firing, owing to removal of impurity oxygen and the like, a highly thermally conductive AlN sintered body can be obtained.

[0021]

[Examples]

Hereinafter, examples of the present invention will be described. The present invention is not limited to the following examples.

Example 1

As a sintering aid, 3.0% by weight of Y_2O_3 was added to an AlN powder with a specific surface area of 12.0 m^2/g, and mixed by a wet type ball mill. The obtained mixture was dried and granulated, then formed

into a disk shape with a diameter of 20 mm and a height of 10 mm by a uniaxial press, and further subjected to CIP with a pressure of 1.5 ton/cm^2 to obtain a disk-shaped formed body.

[0022]

Successively, the obtained formed body was set in a crucible made of BN, covered with a loose cover made of BN, and the crucible was housed in a carbon furnace. While N_2 gas containing 4% of H_2 being circulated, the temperature was raised to 120°C and the gas was changed to 100% N_2. The temperature was further raised to 1650°C and kept for 3 hours to obtain an AlN sintered body.

Example 2

An AlN sintered body was obtained in the same manner as Example 1, except that <u>3% by weight of $Y(NO_3)_3$ is added as a sintering aid in terms of Y_2O_3,</u> and the sintering temperature was changed to be 1600°C.

[0023]

Example 3

As a sintering aid, 3.0% by weight of Y_2O_3 was added to an AlN powder with a specific surface area of 15.0 m^2/g and a disk-shaped formed body was obtained in the same manner as Example 1. After that, the formed body was put in an alumina setter, covered with an aluminum plate and housed in a carbon furnace. While N_2 gas containing 4% of H_2 being circulated, the temperature was raised to 1600°C and kept for 3 hours to obtain an AlN sintered body. N_2 gas containing 4% of H_2 was used for the entire process.

[0024]

Example 4

An AlN sintered body was obtained in the same manner as Example 3, except that Y_2O_3 as a sintering aid was replaced by La_2O_3.

Example 5

An AlN sintered body was obtained in the same manner as Example 3, except that the crucible made of BN and a cover made of BN used in Example 1 were used in place of the alumina setter and the alumina plate, and 100% N_2 was used for the entire process.

[0025]

Comparative Example 1

As a sintering aid, 3.0% by weight of Y_2O_3 was added to an AlN powder with a specific surface area of 10.0 m^2/g and a disk-shaped formed body was obtained in the same manner as Example 1. After that, the formed body was put in a crucible made of BN, covered with a loose cover made of BN, and housed in a carbon furnace. While 100 % N_2 gas being circulated, the temperature was raised to 1650°C and kept for 3 hours to obtain an AlN sintered body.

[0026]

Comparative Example 2

An AlN sintered body was obtained in the same manner as Comparative Example 1, except that 3.0% by weight of Y_2O_3 and 0.5% by weight of CaO were added as the sintering aid.

Comparative Example 3

An AlN sintered body was obtained in the same manner as Comparative Example 2, except that an AlN powder with a specific surface

area of 3.0 m^2/g was used as the AlN powder.

[0027]

Tables 1 and 2 show the main firing conditions of the respective Examples and Comparative Examples, and the densities, the grain sizes, the thermal conductivities and the bending strength of the respective AlN sintered bodies obtained in Examples and Comparative Examples.

[0028]

[Table 1]

	Type and amount of sintering aid (% by weight)	Firing temperature and duration °C, Hr	Atmosphere at firing	Material of container for firing
Example 1	Y_2O_3 3% by weight	1650 3	1200°C or less: $H_2 + N_2$ * 1200°C or more: N_2	BN
Example 2	$Y(NO_3)_3$ 3% by weight	1600 3	1200°C or less: $H_2 + N_2$ * 1200°C or more: N_2	BN
Example 3	Y_2O_3 3% by weight	1600 3	$H_2 + N_2$ *	Al_2O_3
Example 4	La_2O_3 3% by weight	1600 3	$H_2 + N_2$ *	Al_2O_3
Example 5	Y_2O_3 3% by weight	1600 3	N_2	BN
Comparative Example 1	Y_2O_3 3% by weight	1650 3	N_2	BN
Comparative Example 2	Y_2O_3 3% by weight CaO 0.5% by weight	1650 3	N_2	BN
Comparative Example 3	Y_2O_3 3% by weight CaO 0.5% by weight	1650 3	N_2	BN

*: N_2 gas containing 4% of H_2 #: 3% by weight in terms of Y_2O_3

[0029]

[Table 2]

	Density (g/cm^3)	Thermal conductivity (W/mK)	Bending strength (kgf/mm^2)	Average grain size	Specific surface area of AlN powder
Example 1	3.30	150	44	0.9 μm	12 m^2/g
Example 2	3.29	143	46	0.8 μm	12 m^2/g
Example 3	3.30	135	48	0.7 μm	15 m^2/g
Example 4	3.33	130	47	0.7 μm	15 m^2/g
Example 5	3.30	120	50	0.7 μm	15 m^2/g
Comparative Example 1	2.87	100	25	1.0 μm	10 m^2/g
Comparative Example 2	3.23	115	28	1.4 μm	10 m^2/g
Comparative Example 3	3.10	108	23	1.5 μm	3 m^2/g

[0030]

As shown in Table 2, the AlN sintered bodies of Examples were sufficiently densified without using an alkaline earth type or fluoride type sintering aid and provided with both high thermal conductivities and bending strength. On the contrary, AlN sintered bodies of Comparative Examples were not provided with those properties.

[0031]

[Effects of the Invention]

In an AlN sintered body production method according to the present invention, firing is carried out at a low temperature of not more than 1650°C, therefore the life of a container for a firing jig can be prolonged and it is made possible to utilize a container made of an economical material and further power consumption can be saved to result in cost down of running cost as well. Furthermore, since neither alkaline earth compound nor fluoride type sintering aid is required to be used, uneven firing, warping, and deterioration of a furnace and a setter owing to diffusion can be prevented and further the grain size becomes small to give AlN sintered bodies excellent in mechanical strength at a low cost. In addition, in the case reduction treatment is carried out, the thermal conductivities of AlN sintered bodies can be improved. Accordingly, the present invention is practical and remarkably advantageous for practical application.

引例2

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(54)【発明の名称】　窒化アルミニウム焼結体の製造方法

(57)【要約】

【目的】　熱伝導率および機械的強度に優れた窒化アルミニウム焼結体を安価に得られる実用的な方法を提供する。

【構成】　この発明は、比表面積が１２．０ｍ２／ｇ以上の窒化アルミニウム粉末に焼結助剤として非フッ素系の酸素を含む稀土類化合物を添加し成型してある成形体を、非酸化性雰囲気で１６５０℃以下の温度で焼成することを特徴とする。

【特許請求の範囲】
【請求項1】　窒化アルミニウム粉末に焼結助剤を添加し成型してなる成形体を、非酸化性雰囲気で焼成することにより焼結させる窒化アルミニウム焼結体の製造方法において、前記窒化アルミニウム粉末の比表面積が12．0m²／g以上であって、前記焼結助剤が、非フッ化系の酸素を含む稀土類化合物であり、前記非酸化性雰囲気での焼成を1650℃以下の温度で行うことを特徴とする窒化アルミニウム焼結体の製造方法。
【請求項2】　焼成の前後または焼成中に還元処理も行う請求項1記載の窒化アルミニウム焼結体の製造方法。
【発明の詳細な説明】
【0001】
【産業上の利用分野】この発明は、窒化アルミニウム焼結体の製造方法に関する。
【0002】
【従来の技術】ＩＣ等に代表されるような半導体素子の高集積化や大電力化が進み、これに伴って、放熱性の良い電気絶縁材料が要求されるようになった。その中でも、特に、窒化アルミニウム焼結体からなる絶縁基板が、熱伝導性、熱膨張性、電気絶縁性等の点で優れているということから、注目され実用化も進んでいる。
【0003】しかしながら、窒化アルミニウム焼結体は、原料の窒化アルミニウム粉末が高価であるとともに難焼結性で1750℃以上の高温焼成を必要とするため、非常に高価なものとなっていた。このため、焼成温度を下げてコスト低減を図る窒化アルミニウム焼結体の製造方法が提案されている。窒化アルミニウム粉末に、焼結助剤として、稀土類元素のフッ化物や酸化物とアルカリ土類元素のフッ化物又は酸化物とを併用することが提案されている（特開昭61-209959 号公報,USP4,746,637 号明細書）。ここでは、1550～1700℃という低温焼成で緻密で高熱伝導率の窒化アルミニウム焼結体が得られるとされている。　しかしながら、上記の方法の場合、以下のような問題がある。
【0004】焼結助剤にフッ化物を用いると、焼成時に焼結助剤の分解で生じたフッ素元素が簡単にＨＦなどの腐食性・毒性のガスになり、作業者の健康への悪影響や焼成炉等の損傷などの問題が起こるために実用的とは言えない。焼結助剤としての稀土類化合物とアルカリ土類化合物の併用は、稀土類化合物の単独使用の場合に比べ、液相形成温度の低下が認められ、そのため、低温での焼結が可能となるのであるが、同時に液相形成による粒成長が顕著となるため高熱伝導率化には有利でも機械的強度の面では不利となる。また、アルカリ土類の場合、焼成中に拡散が起こり易く、焼結体中で不均一な分布を生じ易く、また、窒化アルミニウム焼結体の焼けムラ、焼成炉や治具であるセッターへの付着反応による劣化などといった問題を生じる。加えて、上記の液相は厚い粒界層を形成してグレインを取り巻くため、破壊モードが粒界破壊となる。一般に機械強度は稀土類化合物単独の場合に比べて低下してしまう。稀土類化合物がY_2O_3単独の場合を例にとると、1760℃でAl_2O_3との間で液相を形成し、この液相が窒化アルミニウムのグレインを濡らしはするのであるが、粒界層を形成せずに粒界の三重点に集まり易くて粒界層は非常に薄くなり、この結果、破壊モードは粒界破壊ではなく粒内破壊となり易い。粒内破壊の方が粒界破壊に比べて、一般的に機械的強度は高くなる。
【0005】
【発明が解決しようとする課題】この発明は、上記事情に鑑み、熱伝導率および機械的強度に優れた窒化アルミニウム焼結体を安価に得ることのできる実用的な方法を提供することを課題とする。
【0006】
【課題を解決するための手段】前記課題を解決するため、この発明にかかる窒化アルミニウム焼結体の製造方法は、窒化アルミニウム粉末に焼結助剤を添加し成型してなる成形体を、非酸化性雰囲気で焼成することにより焼結させるにあたり、窒化アルミニウム粉末に焼結助剤を添加し成型してなる成形体を、非酸化性雰囲気で焼成することにより焼結させる窒化アルミニウム焼結体の製造方法において、前記窒化アルミニウム粉末の比表面積が12．0m²／g以上であって、前記焼結助剤が、非フッ化系の酸素を含む稀土類化合物であり、前記非酸化性雰囲気での焼成を1650℃以下の温度で行うようにしている。
【0007】この発明において、焼成の前後または焼成中に還元処理を行うようにする形態は、以下で詳しく述べるように、得られる窒化アルミニウム焼結体（以下、「ＡｌＮ焼結体」と言う）の熱伝導率の高める上で有効であり、有用な形態ということが出来る。この発明において、比表面積が12．0m²／g以上の微小粒径の窒化アルミニウム粉末（以下、「ＡｌＮ粉末」と言う）を用いる理由は、非フッ化系の酸素を含む稀土類化合物（稀土類元素の含酸素化合物）、すなわち稀土類酸化物，焼成で稀土類酸化物となる非フッ化系の化合物からなる稀土類化合物群の範囲にある化合物だけの使用のもとに1650℃以下の低温焼成で焼結させられるようになるからである。
【0008】前述したように、稀土類元素のフッ化物又は酸化物とアルカリ土類元素のフッ化物又は酸化物を併用すると、比表面積が12．0m²／g未満のＡｌＮ粉末でも焼結可能なのであるが、粒成長などによる機械的強度の低下、ＡｌＮ焼結体の焼けムラ、焼成炉やセッターの劣化等の問題を生じる。この発明は、併用形態をとらずとも、低温焼成で焼結させられるようになる上記併用の不都合が解消できるようになる。
【0009】代表的な稀土類元素の含酸素化合物であるY_2O_3を例にとると、Y_2O_3とＡｌＮ粉末表面のＡ

l_2O_3とで共晶融液を形成するのが、1760℃以上であり、液相焼結を行うには、これ以上の温度で焼成することが必要となる。発明者らの検討によると、比表面積が3．0m²／g程度の粗いAlN粉末を用い、Y_2O_3単独で焼結させようとすると、上述の液相焼結は不可欠であり、1760℃以上の高温焼成が必須となる。そこで、発明者らは、検討を続け、比表面積が12．0m²／g以上の細かなAlN粉末なら液相焼結でなく固相焼結が可能で焼成温度の低減が図れるようであることを見いだしたのである。比表面積が12．0m²／g未満のAlN粉末だと1700℃を越す焼成温度が必要なのであるが、比表面積が12．0m²／g以上のAlN粉末だと非フッ化系稀土類化合物の焼結助剤だけで1650℃以下の焼成温度で焼結が可能であることを見いだしたのである。

【0010】1650℃以下の焼成で焼結が可能となると、焼成コストの低減に反映されるメリットがある。具体的には、焼成容器として使われている高価なBN容器の寿命が大幅に伸びることが挙げられるし、さらに、高価なBN容器の代わりに安価なアルミナ系容器の使用が可能となることも挙げられる。安価なアルミナ系容器は1650℃を超える焼成では高温クリープによる変形が著しくなるため従来なら使えない。さらに、消費電力の節約などで焼成炉のランニングコストの面でもコストダウンが図れる。

【0011】続いて、この発明で得るAlN焼結体の熱伝導率や機械的強度に関して述べる。上でみたように、この発明の場合、比表面積が12．0m²／g以上の微細なしAlN粉末を用い、非フッ化系稀土類化合物の焼結助剤だけで1650℃以下の焼成温度で焼結を行うので、その焼結メカニズムは液相焼結ではなく固相焼結であると考えられるのである。それ故、AlN焼結体のグレインサイズは1650℃以下でも液相を形成するアルカリ土類化合物を焼結助剤として用いた場合に比べ小さく、この結果、機械的強度が大きくなる。ただ、AlN焼結体のグレインサイズが小さくなることで熱伝導率は普通は小さくなる傾向がある。なぜなら、AlN焼結体での熱伝導機構はフォノン伝導であり、このフォノン伝導は粒界部分で散乱を起こし易く、グレインサイズの小さなAlN焼結体の場合は粒界部分が多く、この結果、このフォノン散乱も大きく、熱伝導が妨げられるからである。

【0012】また、熱伝導率低下の原因となるAlN粉末中の不純物酸素は、一般にAlN粉末の比表面積が大きくなる（粒径が細かくなる）ほど増加する。というのは、不純物酸素はAlN粉末の表層に存在するからである。したがって、比表面積が12．0m²／g以上の微細なAlN粉末を用いるこの発明では、不純物酸素量が、必然的に粒径の大きなAlN粉末を用いる場合に比べて多くなる。

【0013】このように、この発明で得るAlN焼結体はグレインサイズが小さいこと、原料のAlN粉末中の不純物酸素の多いことで熱伝導率の点では不利である。しかしながら、この発明において、焼成の前後または焼成中に還元処理がなされるならば、熱伝導率を向上させることが出来る。この還元処理でAlN粉末中の不純物酸素が減り、その分、熱伝導率が高まる。ただ、この還元処理で焼結体でのグレインサイズに変化は殆ど生じないため、グレインサイズによる熱伝導率の減少の解消は全く望めないようにも見えるが、酸素量の低減により焼結時に窒化アルミニウムのグレイン内にAlN粉末の表層の酸素が一部取り込まれ、これによりグレイン自体の熱伝導率が改善されるので、グレインサイズによる熱伝導率の減少の解消も、一定程度は望めることになる。このように、還元処理も行う場合は、グレインサイズは小さいながらも、高純度化により高熱伝導率化が図れるのである。

【0014】上述の要点を簡単に纏めると以下のようなことになる。この発明では、種々の問題の原因となるアルカリ土類化合物やフッ素系の焼結助剤を使わず、経済的な焼成コストを可能とする1650℃以下の低温焼成で焼結させるために、原料として12m²／g以上の微粒子のAlN粉末と稀土類元素の含酸素化合物を用いる。その結果、焼結体中のグレインサイズはアルカリ土類化合物を使った場合と比較して小さくなるため、機械的強度の向上が図れる。また、熱伝導率に関しては還元処理の採用によるAlN粉末の不純物酸素の還元で向上させることが可能となる。

【0015】焼結助剤として使う非フッ素系の稀土類化合物（稀土類元素の含酸素化合物）における稀土類元素としては、Y，La，Dy，Er，Ce，Sm，Pm，NdEu，Gd，Tb，Pr，Tm，Lu，Ho，Ybなどの酸化物，焼成で稀土類酸化物となる化合物としての炭酸化物や硝酸化物、水酸化物、しゅう酸化物などの形態のものが挙げられる。焼結助剤の使用にあたっては、稀土類酸化物を複数種併用したり、焼成で稀土類酸化物となる化合物を複数種併用したり、稀土類酸化物と焼成で稀土類酸化物となる化合物とを併用したりするようにしてもよい。焼結助剤の添加量に関しては、得られるAlN焼結体全体を100重量%とすると、そのうち焼結助剤が0．1～10重量%を占めるようになるようにする。

【0016】焼成は、1400程度から1650℃までの温度範囲で1～6時間程度の時間行うが、この焼成条件に限らない。還元処理は、焼成の前後または焼結のための焼成中のいずれでもよいが、焼結の進んでいない前が酸素が除去され易い。例えば、1650℃で焼結を行う場合、1200℃までを還元雰囲気とし、その後は中性雰囲気で焼結させるようにしてもよいし、全焼成中を還元雰囲気とし焼結処理と還元処理を同時に平行して始

と同じ期間だけ行うようにしてもよい。還元処理に使える還元雰囲気としては、H_2、CO、NH_3、CH_4、C_2H_4、C_2H_6、C_3H_8 等の還元性ガス雰囲気が挙げられ、これらの還元性ガスをN_2、Ar等の中性ガス雰囲気と組み合わせることで効果的な処理雰囲気を実現することができる。さらに、焼成炉がカーボンヒータやカーボン炉材を使用したカーボン炉である場合、蒸気相炭素による還元雰囲気の形成が容易である。

【0017】

【作用】この発明の場合、種々の問題を生じるアルカリ土類化合物やフッ素系の焼結助剤は使わずに、比表面積が12．0m²／g未満のAlN粉末に対して非フッ素系の稀土類化合物の焼結助剤だけを用い、1650℃以下の低温の焼成で焼結させられる。

【0018】焼結助剤としてアルカリ土類化合物やフッ素系のものを使わずにすむため、AlN焼結体の焼けムラ、反り、炉やセッターへの拡散による劣化が阻止される上、1650℃以下の低温の焼成であるため、焼成容器の長寿命化や低価格材料化が可能となるとともに消費電力の節約などのランニングコスト低減も可能となる。

【0019】また、得られるAlN焼結体中のグレインサイズが小さくなるため、機械的強度の向上が達成される。阻止される上、1650℃以下の低温の焼成であるため、焼結用容器の長寿命化や低価格材料化が可能となるとともに消費電力の節約などのランニングコスト低減も可能となる。

【0020】焼成の前後または焼成中の還元処理を行う場合は、不純物酸素の除去などにより、高熱伝導率のAlN焼結体を得られるようになる。

【0021】

【実施例】以下、この発明の実施例を説明する。この発明は下記の実施例に限らない。

－実施例1－

比表面積が12．0m²／gのAlN粉末に、焼結助剤としてし、Y_2O_3 を3．0重量%添加し、湿式ボールミル混合、乾燥整粒の後、一軸プレスにより直径20mm、高さ10mmの円板状に成型したのち、1．5ton/cm² の圧力でCIPを施し、円板状の成形体を得た。

【0022】続いて、この成形体をBN製ルツボ中に入れ、ルーズなBN製フタを被せて、カーボン炉中に収納し、4%のH_2 を含有したN_2 ガスを流しながら1200℃まで昇温した後、ガスを100%N_2 ガスに切替え、1650℃に昇温して3時間保持し、AlN焼結体を得た。

－実施例2－

焼結助剤としてし、Y_2O_3 をY（NO_3）$_3$ に変え、焼結温度を1600℃とした他は、実施例1と同様にしてAlN焼結体を得た。

【0023】－実施例3－

比表面積が15．0m²／gのAlN粉末に、焼結助剤としてし、Y_2O_3 を3．0重量%添加し、実施例1と同様にして円板状の成形体を得たのち、この成形体をアルミナセッター中に入れ、アルミナ板でふたをして、カーボン炉中に収納し、4%のH_2 を含有したN_2 ガスを流しながら1600℃まで昇温して3時間保持し、AlN焼結体を得た。4%のH_2 を含有したN_2 ガスは全工程で使用した。

【0024】－実施例4－

焼結助剤としてし、Y_2O_3 をLa_2O_3 に変えた他は、実施例3と同様にしてAlN焼結体を得た。

－実施例5－

アルミナセッターとアルミナ板の代わりに、実施例1のBN製ルツボとBN製フタを用い、全工程中、100%N_2 ガスを用いるようにした他は、実施例3と同様にしてAlN焼結体を得た。

【0025】－比較例1－

比表面積が10．0m²／gのAlN粉末に、焼結助剤としてし、Y_2O_3 を3．0重量%添加し、実施例1と同様にして円板状の成形体を得たのち、この成形体をBN製ルツボ中に入れ、ルーズなBN製フタを被せて、カーボン炉中に収納し、100%N_2 ガスを流しながら、1650℃に昇温して3時間保持し、AlN焼結体を得た。

【0026】－比較例2－

焼結助剤としてし、Y_2O_3 を3、0重量%およびCaOを0．5重量%添加した他は、比較例1と同様にしてAlN焼結体を得た。

－比較例3－

AlN粉末として、比表面積が3．0m²／gのAlN粉末を用いた他は、比較例2と同様にしてAlN焼結体を得た。

【0027】実施例および比較例における焼成条件の主なもの、実施例および比較例で得られた各AlN焼結体について測定した密度、グレインサイズ、熱伝導率および曲げ強度を、表1、表2に記す。

【0028】

【表1】

	焼結助剤の種類と量（重量%）	焼成温度と時間 ℃, Hr	焼成時雰囲気	焼成用の容器の材質
実施例1	Y_2O_3 3重量%	1650 3	～1200℃ H_2+N_2 ※ 1200℃～ N_2	BN
実施例2	$Y(NO_3)_3$ 3重量%	1600 3	～1200℃ H_2+N_2 ※ 1200℃～ N_2	BN
実施例3	Y_2O_3 3重量%	1600 3	H_2+N_2 ※	Al_2O_3
実施例4	La_2O_3 3重量%	1600 3	H_2+N_2 ※	Al_2O_3
実施例5	Y_2O_3 3重量%	1600 3	N_2	BN
比較例1	Y_2O_3 3重量%	1650 3	N_2	BN
比較例2	Y_2O_3 3重量% CaO 0.5重量%	1650 3	N_2	BN
比較例3	Y_2O_3 3重量% CaO 0.5重量%	1650 3	N_2	BN

※ H_2 4%含有のN_2ガス

【0029】

【表2】

	密度 (g/cm³)	熱伝導率 (W/mK)	曲げ強度 kgf/mm²	平均グレインサイズ	ＡｌＮ粉末の非表面積
実施例１	３．３０	１５０	４４	０．９μm	１２ m²/g
実施例２	３．２９	１４３	４６	０．８μm	１２ m²/g
実施例３	３．３０	１３５	４８	０．７μm	１５ m²/g
実施例４	３．３３	１３０	４７	０．７μm	１５ m²/g
実施例５	３．３０	１２０	５０	０．７μm	１５ m²/g
比較例１	２．８７	１００	２５	１．０μm	１０ m²/g
比較例２	３．２３	１１５	２８	１．４μm	１０ m²/g
比較例３	３．１０	１０８	２３	１．５μm	３ m²/g

【００３０】表２にみるように、実施例のＡｌＮ焼結体は、アルカリ土類系やフッ素系の焼結助剤を使わずとも、十分に緻密化しており、又、高い熱伝導率と曲げ強度を兼ね備えているが、比較例のＡｌＮ焼結体は、これらの特性を兼ね備えてはいなかった。

【００３１】

【発明の効果】この発明にかかるＡｌＮ焼結体の製造方法では、１６５０℃以下の低温焼成であるため、焼成治具用容器の長寿命化および低価格材容器の使用が可能となるとともに消費電力の節約などによるランニングコストの低減も可能となる上、アルカリ土類系やフッ素系の焼結助剤を使わずにすむため、焼けムラ、反り、炉やセッターへの拡散による劣化が防げるだけでなく、グレインサイズが小さくなり、機械的強度に優れたＡｌＮ焼結体が安価に得られ、加えて還元処理が施される場合にはＡｌＮ焼結体の熱伝導率の向上も可能となり、したがって、この発明は実用的であって非常に有用である。

【手続補正書】

【提出日】平成５年２月２４日

【手続補正１】

【補正対象書類名】明細書

【補正対象項目名】全文

【補正方法】変更

【補正内容】

【書類名】明細書

【発明の名称】窒化アルミニウム焼結体の製造方法

【特許請求の範囲】

【請求項１】　窒化アルミニウム粉末に焼結剤を添加し成形してなる成形体を、非酸化性雰囲気で焼成することにより焼結させる窒化アルミニウム焼結体の製造方法において、前記窒化アルミニウム粉末の比表面積が１２．０ｍ２／ｇ以上であって、前記焼結助剤が、非フッ素系の酸素を含む稀土類化合物であり、前記非酸化性雰囲気での焼成を１６５０℃以下の温度で行うことを特徴とする窒化アルミニウム焼結体の製造方法。

【請求項２】焼成の前後または焼成中に還元処理も行う請求項１記載の窒化アルミニウム焼結体の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】この発明は、窒化アルミニウム焼結体の製造方法に関する。

【０００２】

【従来の技術】ＩＣ等に代表されるような半導体素子の高集積化や大電力化が進み、これに伴って、放熱性の良い電気絶縁材料が要求されるようになった。その中でも、特に窒化アルミニウム焼結体からなる絶縁基板が、熱伝導性、熱膨張性、電気絶縁性等の点で優れているということから、注目され実用化も進んでいる。

【０００３】しかしながら、窒化アルミニウムの焼結体は、原料の窒化アルミニウム粉末が高価であるとともに難焼結性で１７５０℃以上の高温焼成を必要とするため、非常に高価なものとなっていた。このため、焼成温度を下げてコスト低減を図る窒化アルミニウム焼成体の製造方法が提案される。窒化アルミニウム粉末に、焼結助剤として、稀土類元素のフッ化物や酸化物とアルカリ土類元素のフッ化物は酸化物とを併用することが提案されている（特開昭６１－２０９９５９号公報、ＵＳＰ４，７４６，６３７号）。ここでは、１５５０～１７００℃という定温焼成で緻密で高熱伝導率の窒化アルミニウム焼結体が得られるとされている。しかしながら、上記の方法の場合、以下のような問題がある。

【０００４】焼結助剤にフッ化物を用いると、焼成時に焼結助剤の分解で生じたフッ素元素が簡単にＨＦなどの腐食性・毒のガスになり、作業者の健康への悪影響や焼成炉等の損傷などの問題が起るために実用的とは言えない。焼結助剤としての稀土類化合物とアルカリ土類化合物の併用は、稀土類化合物の単独使用の場合に比べ、液相形成温度の低下が認められ、そのため、低温での焼結が可能となるのであるが、同時に液相形成による粒成長が顕著のなるため高熱伝導率化には有利でも機械的強度の面では不利となる。また、アルカリ土類の場合、焼成中に拡散が起り易く、焼結体中で不均一な分布を生じ易く、また、窒化アルミニウム焼結体の焼けムラ、焼成炉や治具であるセッターへの付着反応による劣化などといった問題を生じる。加えて、上記の液相は厚い粒界層を形成してグレインを取り巻くため、破壊モードが粒界破壊となる。一般に機械強度は稀土類化合物単独の場合に比べて低下してしまう。稀土類化合物がＹ２０２単独の場合を例にとると、１７６０℃でＡ１２０３との間で液相を形成し、この液相が窒化アルミニウムのグレインを濡らしはするのであるが、アルカリ土類のように厚い粒界層を形成せずに粒界の三重点に集まり易くて粒界層は非常に薄くなり、この結果、破壊モードは粒界破壊ではなく粒内破壊となり易い。粒内破壊の方が粒界破壊に比べて、一般的に機械的強度は高くなる。

【０００５】

【発明が解決しようとする手段】この発明は、上記事情に鑑み、熱伝導率および機械的強度に優れた窒化アルミニウム焼結体を安価に得ることのできる実用的な方法を提供することを課題とする。

【０００６】

【課題を解決するための手段】前記課題を解決するため、この発明にかかる窒化アルミニウム焼結体の製造方法は、窒化アルミニウム粉末に焼結助剤を添加し成型してなる成形体を、非酸化性雰囲気で焼成することにより焼結させるにあたり、前記窒化アルミニウム粉末の比表面積が１２．０ｍ２／ｇ以上であって、前記焼結助剤が、非フッ素系の酸素を含む稀土類化合物であり、前記非酸化性雰囲気での焼成を１６５０℃以下の温度で行うようにしている。

【０００７】この発明において、焼成の前後または焼成中に還元処理を行うようにする形態は、以下詳しく述べるように、得られる窒化アルミニウム焼結体（以下、「ＡｌＮ焼結体」と言う）の熱伝導率を高める上で有効であり、有用な形態ということが出来る。この発明において、比表面積が１２．０ｍ２／ｇ以上の微小粒径の窒化アルミニウム粉末（以下、「ＡｌＮ粉末」と言う）を用いる理由は、非フッ素系の酸素を含む稀土類化合物（稀土類元素の含酸素化合物）、すなわち稀土類化合物、焼成で稀土類化合物となる非フッ素系の化合物からなる稀土類化合物群の範囲にある化合物だけの使用のもとに１６５０℃以下の低温焼成で焼結させられるようになるからである。

【０００８】前述したように、稀土類元素のフッ化合物又は酸化物とアルカリ土類元素のフッ化物又は酸化物を併用すると、比表面積が１２．０ｍ２／ｇ未満のＡｌＮ粉末でも焼結可なのであるが、粒成長などによる機械的強度の低下、ＡｌＮ焼結体の焼けムラ、焼成炉やセッターの劣化等の問題を生じる。この発明は、併用形態をとらずとも、低温焼成で焼結させられるようになる上記併用の不都合が解消できるようになる。

【０００９】代表的な稀土類元素の含酸素化合物であるＹ２０２を例にとると、Ｙ２０３とＡｌＮ粉末表面のＡｌ２０３とで共晶融液を形成するのが、１７６０℃以上であり、液相焼結を行うには、これ以上の温度で焼成することが必要となる。発明者らの検討によると、比表面積が３．０ｍ２／ｇ程度の粗いＡｌＮ粉末を用い、Ｙ２０３単独で焼結させようとすると、上述の液相焼結は不可欠であり、１７６０℃以上の高温焼成が必須となる。そこで、発明者らは、検討を続け、ＡｌＮ粉末の粒径をさらに細かくしてゆくと液相焼結でなく固相焼結が可能で焼成温度の低減が図れるようであことを見いだしたのである。比表面積が１２．０ｍ２／ｇ未満のＡｌＮ粉末だと１７００℃を越す焼成温度が必要なのであるが、比表面積が１２．０ｍ２／ｇ以上のＡｌＮ粉末だと非フッ素系稀土類化合物の焼結助剤だけで１６５０℃以下の焼成温度で焼結が可能であることを見いだしたのである。

【００１０】１６５０℃以下の焼成で焼結が可能となると、焼成コストの低減に反映されるメリットがある。具体的には、焼成容器として使われている高価なＢＮ容器の寿命が大幅に伸びることが挙げられるし、さらに、高価なＢＮ容器の代わりに安価なアルミ系容器の使用が可能となることも挙げられる。安価なアルミナ系容器は１６５０℃を超える焼成では高温クリープによる変形が著しくなるため従来なら使えない。さらに、消費電力の節約などで焼成炉のランニングコストの面でもコストダウンが図れる。

【００１１】続いて、この発明で得るＡｌＮ焼結体の熱

伝導率や機械的強度に関して述べる。上で述べたように、この発明の場合、比表面積が１２．０ｍ２／ｇ以上の微細なＡｌＮ粉末を用い、非フッ素系稀土類化合物の焼結助剤だけで１６５０℃以下の焼成温度で焼結を行うので、その焼結メカニズムは液相焼結ではなく固相焼結であると考えられるのである。それ故、ＡｌＮ焼結体のグレインサイズは１６５０℃以下でも液相を形成するアルカリ土類化合物を焼結助剤として用いた場合に比べ小さく、この結果、機械的強度が大きくなる。ただ、ＡｌＮ焼結体のグレインサイズが小さくなることで熱伝導率は普通は小さくなる傾向がある。なぜなら、ＡｌＮ焼結体での熱伝導機構はフォノン伝導であり、このフォノン伝導は粒界部分で散乱を起こし易く、グレインサイズの小さなＡｌＮ焼結体の場合は粒界部分が多く、この結果、このフォノン散乱も大きく、熱伝導が妨げられるからである。

【００１２】また、熱伝導率低下と原因となるＡｌＮ粉末中の不純物酸素は、一般にＡｌＮ粉末の比表面積が大きくなる（粒径が細かくなる）ほど増加する。というのは、不純物酸素はＡｌＮ粉末の表層に存在し易いからである。したがって、比表面積が１２．０ｍ２／ｇ以上の微細なＡｌＮ粉末を用いるこの発明では、不純物酸素量が、必然的に粒径の大きなＡＮ粉末を用いる場合に比べて多くなる。

【００１３】このように、この発明で得るＡｌＮ焼結体はグレインサイズが小さいこと、原料のＡｌＮ粉末中の不純物酸素の多いことで、熱伝導率の点では不利である。しかしながら、この発明において、焼成の前後または焼成中に還元処理がなされるならば、熱伝導率を向上させることが出来る。この還元処理でＡｌＮ粉末中の不純物酸素が減り、その分、熱伝導率が高まる。すなわち、不純物酸素を減じても、基本的には焼結体のグレインサイズに変化は余り生じないため、やはり、グレンサイズによる熱伝導率の減少の解消、つまり高熱伝導化には不利ではあるが、一方、焼結時にＡｌＮグレイン内にＡｌＮ粒子表層の酸素が一部取り込まれてしまうことによるＡｌＮグレインそのものの熱伝導率の低下は、還元処理による酸素量の低減により緩和される。そのため、グレインサイズは小さいながらも、高純度化により高熱伝導率が達成でき、効果的には、グレンサイズによる熱伝導率の減少の解消につながるのである。

【００１４】上述の要点を簡単にまとめると以下のようなことになる。この発明では、種々の問題の原因となるアルカリ土類化合物やフッ素系の焼結助剤を使わず、経済的な焼成コストを可能とする１６５０℃以下の低温焼成で焼結させるために、原料として１２ｍ２／ｇ以上の微粒子のＡｌＮ粉末と稀土類元素の含酸素化合物を用いる。その結果、焼結体中のグレインサイズはアルカリ土類化合物を使った場合の比較して小さくなるため、機械的強度の向上が図れる。また、熱伝導率に関しては還元処理の採用によるＡｌＮ粉末の不純物酸素の還元で向上させることが可能となる。

【００１５】焼結助剤として使う非フッ素系の稀土類化合物（稀土類元素の含酸素化合物）における稀土類元素としてはＹ，Ｌａ，Ｄｙ，Ｅｒ，Ｃｅ，Ｓｍ，Ｐｍ，Ｎｄ，Ｅｕ，Ｇｄ，Ｔｂ，Ｐｒ，Ｔｍ，Ｌｕ，Ｈｏ，Ｙｄなどの酸化物、焼成で稀土類酸化物となる化合物としての炭酸化物、硝酸化物、水酸化物、しゅう酸化物などの形態のものが挙げられる。焼結助剤の使用にあたっては、稀土類酸化物を複数種併用したり、焼成で稀土類酸化物となる化合物を複数種併用したり、稀土類酸化物と焼成で稀土類酸化物となる化合物を併用したりするようにしてもよい。焼結助剤の添加量に関しては、得られるＡｌＮ焼結体全体を１００重量％とすると、そのうち焼結助剤が０．１～１０重量％を占めるようになるようにする。

【００１６】焼成は、１４００℃程度から１６５０℃までの温度範囲で１～６時間程度の時間行うが、この焼成条件に限らない。還元処理は、焼成の前後または焼結のための焼成中のいずれでもよいが、焼結の進んでいない前が酸素が除去され易い。例えば、１６５０℃で焼結を行う場合、１２００℃までを還元雰囲気とし、その後は中性雰囲気で焼結させるようにしてもよいし、全焼成中を還元雰囲気とし焼結処理と還元処理を同時に平行して殆ど同じ期間だけ行うようにしてもよい。還元処理に使える還元雰囲気としは、Ｈ２，ＣＯ，ＮＨ３，ＣＨ４，Ｃ２Ｈ４，Ｃ２Ｈ６，Ｃ３Ｈ８等の還元性ガス雰囲気が挙られ、これらの還元性ガスをＮ２，Ａｒ等の中性ガス雰囲気と組み合わせることで効果的な処理雰囲気を実現することができる。さらに、焼成炉がカーボンヒータやカーボン炉材を使用したカーボン炉である場合、蒸気相炭素による還元雰囲気の形成が容易である。

【００１７】

【作用】この発明の場合、種々の問題を生じるアルカリ土類化合物よフッ素系の焼結助剤は使わずに、比表面積が１２．０ｍ２／ｇ以上のＡｌＮ粉末に対して非フッ素系の稀土類化合物の焼結助剤だけを用い、１６５０℃以下の低温の焼成で焼結させられる。

【００１８】焼結助剤としてアルカリ土類化合物やフッ素系のものを使わずにすむため、ＡｌＮ焼結体の焼けムラ、反り、炉やセッターへの拡散による劣化が阻止される上、１６５０℃以下の低温の焼成であるため、焼成容器の長寿命化や低価格材料化が可能となるとともに消費電力の節約などのランニングコスト低減も可能となる。

【００１９】また、得られるＡｌＮ焼結体中のグレインサイズが小さくなるため、機械的強度の向上が達成される。

【００２０】焼成の前後または焼成中の還元処理を行う場合は、不純物酸素の除去などにより、高熱伝導率のＡｌＮ焼結体を得られるようになる。

【００２１】

【実施例】以下、この発明の実施例を説明する。この発明は下記の実施例に限らない。

－実施例１－

比表面積が１２．０ｍ２／ｇのＡｌＮ粉末に、焼結助剤として、Ｙ２Ｏ３を３．０重量％添加し、湿式ボールミル混合、乾燥整粒の後、一軸プレスにより直径２０ｍｍ、高さ５ｍｍの円板状に成型したのち、１．５ｔｏｎ／ｃｍ２の圧力でＣＩＰを施し、円板状の成形体を得た。

【００２２】続いて、この成形体をＢＮ製ルツボ中に入れ、ルーズなＢＮ製フタを被せて、カーボン炉中に収納し、４％のＨ２を含有したＮ２ガスを流しながら１２００℃まで昇温した後、ガスを１００％Ｎ２ガスに切替え１６５０℃に昇温して３時間保持し、ＡｌＮ焼結体を得た。

－実施例２－

焼結助剤として、Ｙ（ＮＯ３）３をＹ２Ｏ３換算で３重量％添加し、焼結温度を１６００℃とした他は実施例１と同様にしてＡｌＮ焼結体を得た。

【００２３】－実施例３－

比表面積が１５．０ｍ２／ｇのＡｌＮ粉末に、焼結助剤として、Ｙ２Ｏ３を３．０重量％添加し、実施例１と同様にして円板状の成形体を得たのち、この成形体をアルミセッター中に入れ、アルミナ板でふたをして、カーボン炉中に収納し、４％のＨ２を含有したＮ２ガスを流しながら１６００℃まで昇温して３時間保持し、ＡｌＮ焼結体を得た。４％のＨ２を含有したＮ２ガスは全工程で使用した。

【００２４】－実施例４－

焼結助剤として、Ｙ２Ｏ３をＬａ２Ｏ３に変えた他は、実施例３と同様にしてＡｌＮ焼結体を得た。

－実施例５－

アルミセッターとアルミナ板の代わりに、実施例１のＢＮ製ルツボとＢＮ製フタを用い、全工程中、１００％Ｎ２ガス用いるようにした他は、実施例３と同様にしてＡｌＮ焼結体を得た。

【００２５】－比較例１－

比表面積が１０．０ｍ２／ｇのＡｌＮ粉末に、焼結助剤として、Ｙ２Ｏ３を３．０重量％添加し、実施例１と同様にして円板状の成形体を得たのち、この成形体をＢＮ製ルツボ中に入れ、ルーズなＢＮ製フタを被せて、カーボン炉中に収納し、１００％Ｎ２ガスを流しながら、１６５０℃に昇温して３時間保持し、ＡｌＮ焼結体を得た。

【００２６】－比較例２－

焼結助剤として、Ｙ２Ｏ３を３．０重量％およびＣａＯを０．５重量％添加した他は、比較例１と同様にしてＡｌＮ焼結体を得た。

－比較例３－

ＡｌＮ粉末として、比表面積が３．０ｍ２／ｇのＡｌＮ粉末を用いた他は、比較例２と同様にしてＡｌＮ焼結体を得た。

【００２７】実施例および比較例における焼結条件の主なもの、実施例および比較例で得られた各ＡｌＮ焼結体について測定した密度、グレインサイズ、熱伝導率および曲げ強度を、表１，表２に記す。

【００２８】

【表１】

	焼結助剤の種類と量（重量%）	焼成温度と時間 ℃，Hr	焼成時雰囲気	焼成用の容器の材質
実施例1	Y_2O_3 3重量%	1650 3	～1200℃ H_2 ＋N_2 ※ 1200℃～ N_2	BN
実施例2	$Y(NO_3)_3$ ＃3重量%	1600 3	～1200℃ H_2 ＋N_2 ※ 1200℃～ N_2	BN
実施例3	Y_2O_3 3重量%	1600 3	H_2 ＋N_2 ※	Al_2O_3
実施例4	La_2O_3 3重量%	1600 3	H_2 ＋N_2 ※	Al_2O_3
実施例5	Y_2O_3 3重量%	1600 3	N_2	BN
比較例1	Y_2O_3 3重量%	1650 3	N_2	BN
比較例2	Y_2O_3 3重量% CaO 0.5重量%	1650 3	N_2	BN
比較例3	Y_2O_3 3重量% CaO 0.5重量%	1650 3	N_2	BN

※ H_2 4%含有のN_2ガス　＃ Y_2O_3換算で3重量%

【0029】

【表2】

	密度 (g/cm³)	熱伝導率 (W/mK)	曲げ強度 kgf/mm²	平均グレインサイズ	ＡｌＮ粉末の比表面積
実施例1	３．３０	１５０	４４	０．９μm	１２ m²/g
実施例2	３．２９	１４３	４６	０．８μm	１２ m²/g
実施例3	３．３０	１３５	４８	０．７μm	１５ m²/g
実施例4	３．３３	１３０	４７	０．７μm	１５ m²/g
実施例5	３．３０	１２０	５０	０．７μm	１５ m²/g
比較例1	２．８７	１００	２５	１．０μm	１０ m²/g
比較例2	３．２３	１１５	２８	１．４μm	１０ m²/g
比較例3	３．１０	１０８	２３	１．５μm	３ m²/g

【００３０】表２にみるように、実施例のＡｌＮ焼結体は、アルカリ土類系やフッ素系の焼結助剤を使わずとも、十分に緻密化しており、又、高い熱伝導率の曲げ強度を兼ね備えているが、比較例のＡｌＮ焼結体は、これらの特性を兼ね備えてはいなかった。

【００３１】

【発明の効果】この発明にかかるＡｌＮ焼結体の製造方法では、１６５０℃以下の低温焼成であるため、焼成治具容器の長寿命化および低価格材容器の使用が可能となるとともに消費電力の節約などによるランニングコストの低減も可能となる上、アルカリ土類系やフッ素系の焼結助剤を使わずにすむため、焼けムラ、反り、炉やセッターへの拡散による劣化が防げるだけでなく、グレインサイズが小さくなり、機械的強度に優れたＡｌＮ焼結体が安価に得られ、加えて還元処理が施される場合にはＡｌＮ焼結体の熱伝導率の向上も可能となり、したがって、この発明は実用的であって非常に有用である。

フロントページの続き

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